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Difunctional Monomers based on Perfluoropropylene Telomers

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# Difunctional Monomers Based on Perfluoropropylene Telomers

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Telomers of perfluoropropylene with  $\alpha,\omega$ -diiodoperfluoroalkanes were converted to branched-chain difunctional condensation monomers. The reaction of ethylene with the telomers gave  $\alpha,\omega$ -bis(iodoethyl)perfluoroalkanes, which were converted to the corresponding diols by reaction with fuming sulfuric acid. The reaction of the branched-chain  $\alpha,\omega$ -bis(iodoethyl)-perfluoroalkanes with sodium azide gave the corresponding  $\alpha,\omega$ -bis-(azidoethyl)-perfluoroalkanes. Hydrogenation of the  $\alpha,\omega$ -bis-(azidoethyl)-perfluoroalkanes gave diamines. Phosgenation of the amino groups gave diisocyanates.

## Introduction

Telechelic oligomers allow the convenient tailoring of a broad range of polymer properties,<sup>1-3</sup> and fluorinated examples are of specific interest because of the thermal stability, dielectric properties and biological inertness imparted by fluorine.<sup>4</sup> One of the most useful entries to difunctional fluorocarbon derivatives is the reaction of tetrafluoroethylene with iodine to give  $\alpha,\omega$ -diiodoperfluoroalkanes.<sup>5,6</sup> Although per-

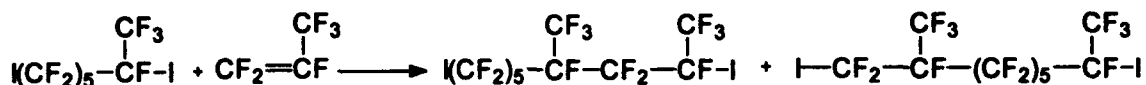
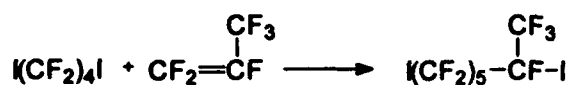
fluoroalkyl iodides are not subject to normal displacement reactions, the compounds can be reacted with ethylene<sup>7,8</sup> to give  $R_FCH_2CH_2I$  groups. The iodines of ethylene adduct of linear diiodoperfluoroalkanes have been converted to hydroxy,<sup>9,10</sup> amino,<sup>11</sup> or isocyanate groups.<sup>11</sup> For polymer applications in which high fluorine content is required, long chain length for these difunctional components is desired, but the properties of the materials approach that of PTFE with increasing chain length; solubility decreases and melting point increases to the point that processing becomes difficult.

A method of improving the processibility of long-chain fluorocarbons is to introduce chain branching. Hauptschein and co-workers<sup>12</sup> reported in 1957 that the reaction of monofunctional perfluoroalkyl iodides with perfluoropropylene gave telomers,  $R_F[CF_2CF(CF_3)]_nI$  ( $n = 1-15$ ). These telomers were oils. Recently,<sup>13</sup> the telomerization with perfluoropropylene has been extended to  $\alpha,\omega$ -diiodoperfluoroalkanes. In the present study, the functionalization of perfluorinated branched diiodides was examined with the objective of obtaining readily processable condensation monomers that can give elastomeric fluorinated polymers.

### Results and Discussion

The reaction of 1,4-diiodoperfluorobutane with perfluoropropylene was carried out at 200 °C, and the product mixture was separated by spinning band distillation. The degree of telomerization was dependent on reaction conditions, with higher temperatures and longer reaction times favoring the formation of higher telomers. The reaction evidently takes place in a stepwise fashion. The 1:1 adduct, 1,6-diiodoper-

fluoroheptane, was isolated but higher oligomers consisted of inseparable isomeric mixtures; reaction of the 1:1 adduct with additional perfluoropropylene can take place at either end of the molecule.



The same reaction conditions were used for the addition of 1,6-diiodoperfluorohexane to perfluoropropylene. The monoadduct, 1,8-diiodoperfluorononane, was isolated in 33% yield, and the isolation of higher oligomers was not investigated.

Ethylene insertion of the branched perfluorodiiiodides was carried out at 160 °C at 250-300 psi. Yields of the perfluoroalkylene  $\alpha,\omega$  bis(iodoethyl) derivatives were 88-95%. Under these conditions, the formation of monoethylene adducts or further ethylene addition to  $-\text{CH}_2\text{CH}_2\text{I}$  groups was not observed. The reactions are summarized in Table 1.



Table 1. Ethylene insertion reactions

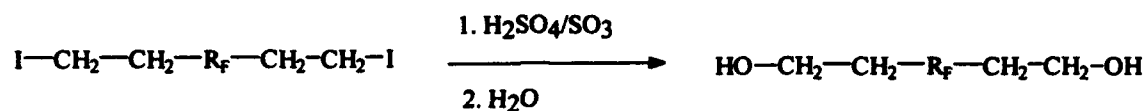
Starting material	Product	Yield
$\text{I}(\text{CF}_2)_5\text{CF}(\text{CF}_3)\text{I}$	$\text{ICH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}(\text{CF}_3)\text{CH}_2\text{CH}_2\text{I}$	93%
$\text{I}[\text{CF}(\text{CF}_3)\text{CF}_2]_x(\text{CF}_2)_4[\text{CF}(\text{CF}_3)\text{CF}_2]_y\text{I}$ $x+y = 2$	$\text{I}(\text{CH}_2)_2[\text{CF}(\text{CF}_3)\text{CF}_2]_x(\text{CF}_2)_4[\text{CF}(\text{CF}_3)\text{CF}_2]_y(\text{CH}_2)_2\text{I}$ $x+y = 2$	90%
$\text{I}[\text{CF}(\text{CF}_3)\text{CF}_2]_x(\text{CF}_2)_4[\text{CF}(\text{CF}_3)\text{CF}_2]_y\text{I}$ $x+y = 3$	$\text{I}(\text{CH}_2)_2[\text{CF}(\text{CF}_3)\text{CF}_2]_x(\text{CF}_2)_4[\text{CF}(\text{CF}_3)\text{CF}_2]_y(\text{CH}_2)_2\text{I}$ $x+y = 3$	95%
$\text{I}(\text{CF}_2)_7\text{CF}(\text{CF}_3)\text{I}$	$\text{ICH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}(\text{CF}_3)\text{CH}_2\text{CH}_2\text{I}$	88%

**Diols.** Linear fluorinated diols of the structure

$\text{HOCH}_2\text{CH}_2(\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$  have been prepared by the reaction of the corresponding bis(2-iodoethyl)perfluoroalkanes with fuming sulfuric acid<sup>10</sup> or with amides.<sup>14,15</sup> The reaction of  $\text{ICH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}(\text{CF}_3)\text{CH}_2\text{CH}_2\text{I}$  with N-methylformamide, followed by hydrolysis of the intermediate ester, gave a mixture of the desired diol and elimination products,  $\text{HOCH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}(\text{CF}_3)\text{CH}=\text{CH}_2$  and  $\text{CH}_2=\text{CH}(\text{CF}_2)_5\text{CF}(\text{CF}_3)\text{CH}=\text{CH}_2$ , from which impure diol could be isolated in only 37% yield.

Subsequently, elimination was avoided by carrying out the conversion of branched bis(2-iodoethyl)perfluoroalkanes to diols in acidic media. The iodides reacted with fuming sulfuric acid at 65 °C, and hydrolysis of the intermediate sulfate esters gave the diols in 73-83% yield. Elimination products were not observed, and the diols were isolated by distillation. The diols were low-melting solids or oils. The prepara-

tions of diols from the corresponding diiodides using fuming sulfuric acid are summarized in Table 2.



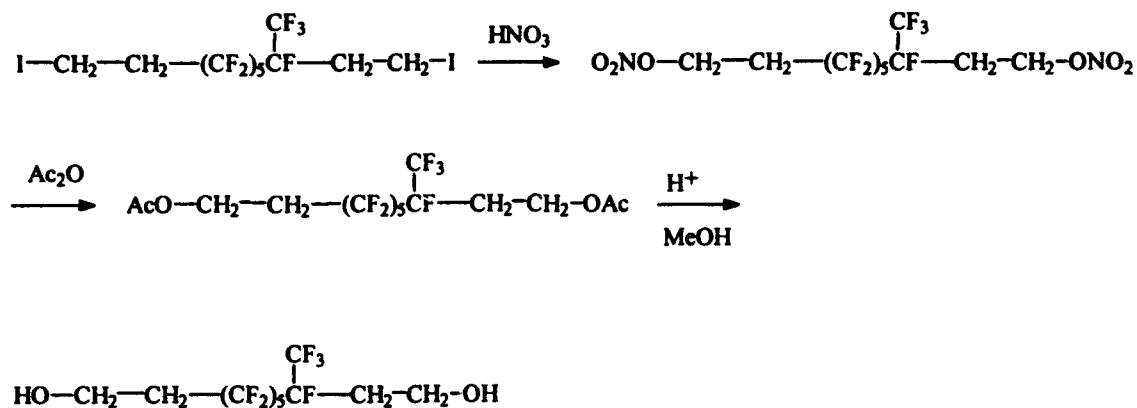
The use of chlorosulfonic acid in place of fuming sulfuric acid did not give satisfactory results. The diol was contaminated with substantial amounts of chloroethyl-containing materials that could not be separated readily.

Table 2. Synthesis of Diols

Starting material	Product	Yield
$\text{ICH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}(\text{CF}_3)\text{CH}_2\text{CH}_2\text{I}$	$\text{HOCH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}(\text{CF}_3)\text{CH}_2\text{CH}_2\text{OH}$	83%
$\text{I}(\text{CH}_2)_x\text{CF}(\text{CF}_3)\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$ $x+y = 2$	$\text{HO}(\text{CH}_2)_x\text{CF}(\text{CF}_3)\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{OH}$ $x+y = 2$	76%
$\text{I}(\text{CH}_2)_x\text{CF}(\text{CF}_3)\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$ $x+y = 3$	$\text{HO}(\text{CH}_2)_x\text{CF}(\text{CF}_3)\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{OH}$ $x+y = 3$	73%
$\text{I}(\text{CF}_2)_7\text{CF}(\text{CF}_3)\text{I}$	$\text{HOCH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}(\text{CF}_3)\text{CH}_2\text{CH}_2\text{OH}$	73%

An alternate method for converting the diiodides to diols based on nitrate intermediates was investigated briefly. Thus, the nitration<sup>16</sup> of  $\text{ICH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}(\text{CF}_3)\text{CH}_2\text{CH}_2\text{I}$  with 100% nitric acid to the dinitrate ester, transesterification with acetic anhydride to the diacetate, and hydrolysis gave the diol in

52% overall yield. The lower yield and extra processing steps make this method less attractive than the fuming sulfuric acid method. The preparation of polyurethanes based on these diols has been reported.<sup>17</sup>

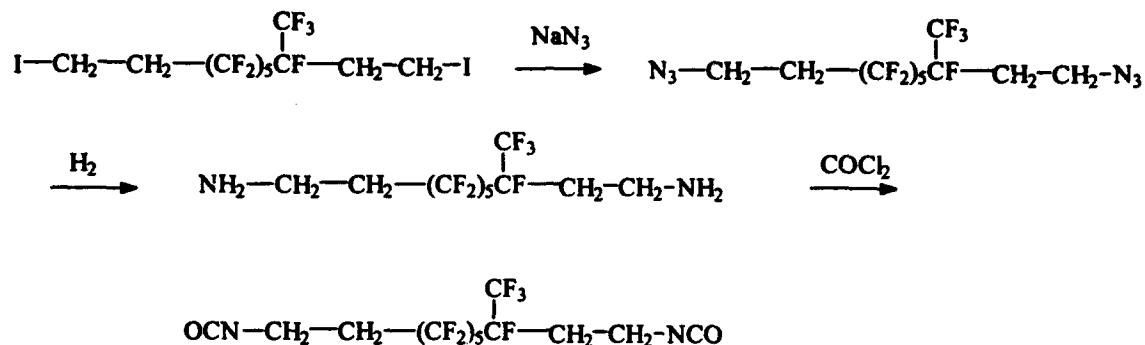


**Diamines and Diisocyanates.** Linear fluorinated diamines of the structure  $\text{NH}_2\text{CH}_2\text{CH}_2-(\text{CF}_2)_n-\text{CH}_2\text{CH}_2\text{NH}_2$  were previously prepared by the displacement of the corresponding diiodides with azide, followed by reduction, and the amines were converted to diisocyanates by phosgenation.<sup>11</sup> The same methods were applied in the present work to the preparation of branched fluorocarbon analogs.

Elimination of HI in the azide displacement step was a major problem. The amount of olefinic materials formed, based on glc analysis, amounted to 30% of the product when DMF was used as the solvent, and 25% with moist acetonitrile. With DMSO as the reaction solvent, 20% elimination was observed, and with a DMSO-THF mixture the elimination side reaction was reduced to 13%. The 1:1 and 1:2 perfluorodiiodobutane-perfluoropropylene telomers were converted to the corresponding



diazides in 55-56 % yields. By comparison, the reaction of sodium azide with linear bis(2-iodoethyl)perfluoroalkanes in DMSO resulted in less than 2% elimination.<sup>11</sup>



The diazides were converted to the corresponding diamines by catalytic reduction<sup>18</sup> or by hydrazine-mediated catalytic transfer hydrogenation.<sup>19</sup> The diamines based on the 1:1 and 1:2 telomers were obtained in 39 and 35% yields, respectively. Conversion of the former diamine to the diisocyanate was achieved in 51% yield by reacting the hydrochloride salt in *o*-dichlorobenzene with phosgene at 135 °C.

## Experimental Section

**Telomerization of 1,4-Diiodoperfluorobutane with Perfluoropropylene.** A mixture of 1,4-diiodoperfluorobutane (20 g, 44 mmol) and perfluoropropylene (35 g, 233 mmol) was heated in a stainless steel pressure cylinder at 200 °C for 77 h. The cylinder was cooled to -78 °C, vented, and allowed to warm to room temperature. The resulting pink oil (31 g) was distilled through a 6" spinning band column to give 6.4 g (24%) of 1,6-diiodoperfluoroheptane, bp 38-40 °C (0.3 mm): <sup>19</sup>F NMR (neat) δ -

62.4 (2 F), -76.0 (3 F), -109.6 (2 F), -115.2 (2 F), -121.2 (2 F), -122.8 (2 F) and -145.6 (1 F). *Anal.* Calcd for  $C_7F_{14}I_2$ : C, 13.92; F, 44.05. Found: C, 13.64; F, 44.01. Further distillation gave 10.1 g (31%) of a mixture of 1:2 telomers, bp 58-60 °C (0.3 mm). A sample of the major component,  $ICF(CF_3)(CF_2)_6CF(CF_3)I$ , was isolated by preparative glc:  $^{19}F$  NMR ( $CDCl_3$ )  $\delta$  -76.0 (6 F), -110.0 (4 F), -121.2 (4 F), -123.6 (4 F) and -146.0 (2 F). *Anal.* Calcd for  $C_{10}F_{20}I_2$ : C, 15.93; F, 50.40. Found: C, 15.83; F, 50.47. Another distillation fraction, 5.0 g (13%), bp 105-108 °C (0.3 mm), consisted of a mixture of 1:3 telomers. *Anal.* Calcd for  $C_{13}F_{26}I_2$ : C, 17.27; F, 54.65. Found: C, 16.99, F, 54.20.

**Telomerization of 1,4-Diiodoperfluorohexane with Perfluoropropylene.** A mixture of 1,4-diiodoperfluorohexane (100 g, 0.18 mol) and perfluoropropylene (153 g, 1.02 mol) was heated in a stainless steel pressure cylinder at 190 °C for 25 hours. The cylinder was cooled to -78 °C, vented, and allowed to warm to room temperature to give 137 g of telomeric iodides. Spinning band distillation gave 43 g (33%) of 1,8-diiodoperfluorononane, bp 60 °C (0.5 mm):  $^{19}F$  NMR  $\delta$  -61.33 (2 F), -75.45 (3 F), -109.64 (2 F), 115.24 to -116 (2 F), 121.83 to -124.05 (8 F), and -147.32 (1 F). *Anal.* Calcd for  $C_9F_{16}I_2$ : C, 15.36; F, 48.58. Found: C, 15.72; F, 48.55. The isolation of higher telomers was not attempted.

**1,10-Diiodo-3-trifluoromethyl-3,4,4,5,5,6,6,7,7,8,8-undecafluorodecane.** A 150-mL stainless steel pressure cylinder was charged with the 1,6-diiodoperfluoroheptane,  $I(CF_2)_5CF(CF_3)I$  (9.4 g, 15.6 mmol) and pressurized to 300 psi with ethylene, and the mixture was heated at 160 °C for 48 h. The cylinder was cooled and vented. The product was dissolved in methylene chloride, washed with aqueous sodium sulfite

and brine, and dried ( $\text{MgSO}_4$ ). The solvent was removed under reduced pressure to give 9.6 g (93%) of 1,10-diiodo-3-trifluoromethyl-3,4,4,5,5,6,6,7,7,8,8-undecafluorodecane, an oil:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.75 (m, 4 H) and 3.28 (m, 4 H);  $^{19}\text{F}$  NMR  $\delta$  -74.5 (3 F), -115.2 (2 F), -117.5 (2 F), -121.0 to -121.6 (4 F), -123.6 (2 F) and -182.8 (1 F). *Anal.* Calcd for  $\text{C}_{11}\text{H}_8\text{F}_{14}\text{I}_2$ : C, 20.02; H, 1.22; F, 40.30. Found: C, 20.05; H, 1.25; F, 40.41.

**Reaction of Ethylene with 1:2 1,4-Diiodoperfluorobutane-Perfluoropropylene Telomers.** The above procedure with a mixture of 1:2 telomers of 1,4-diiodoperfluorobutane and perfluoropropylene (5.6 g, 7.4 mmol) gave 5.4 g (90%) of colorless oil:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.28 (m, 4 H) and 2.81 (m, 4 H);  $^{19}\text{F}$  NMR  $\delta$  -70.2, -74.5, -115.2, -117.5, -120.0, -120.8, -121.6, -123.6, and -182.7; *Anal.* Calcd for  $\text{C}_{14}\text{H}_8\text{F}_{20}\text{I}_2$ : C, 20.75; H, 1.00; F, 46.90. Found: C, 20.76; H, 1.01; F, 46.98.

**Reaction of Ethylene with 1:3 of 1,4-Diiodoperfluorobutane- Perfluoropropylene Telomers.** The above procedure with a mixture of 1:3 1,4-diiodoperfluorobutane-perfluoropropylene telomers (52 g, 57.5 mmol) gave 52.4 g (95%) of colorless oil:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.23 (m, 4 H) and 2.78 (tt, 4 H);  $^{19}\text{F}$  NMR  $\delta$  -70.3 to -74.53 (9 F), -110.1 to -122.4 (14 F), and -178.5 to -183 (3 F). *Anal.* Calcd for  $\text{C}_{17}\text{H}_8\text{F}_{26}\text{I}_2$ : C, 21.27; H, 0.80. Found: C, 21.27; H, 0.80.

**3-Trifluoromethyl-3,4,4,5,5,6,6,7,7,8,8-undecafluorodecane-1,10-diol.** 1,10-Diiodo-3-trifluoromethyl-3,4,4,5,5,6,6,7,7,8,8-undecafluorodecane (20.0 g, 30.3 mmol) was added over a 15 min period to 175 mL of 30% fuming sulfuric acid and the mixture was heated at 65 °C for 23 h. The reaction mixture was poured onto ice. Sodium sulfite was added until the iodine color was discharged and the mixture was

heated at 85 °C for 22 h. The product was extracted with diethyl ether and the organic phase was washed with water, aqueous sodium sulfite, aqueous sodium carbonate and brine. The organic layer was dried ( $\text{MgSO}_4$ ) and Kugelrohr distilled (100 °C, 0.2 mm) to give 11.1 g (83%) of 3-trifluoromethyl-3,4,4,5,5,6,6,7,7,8,8-undecafluorodecane-1,10-diol, an oil:  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  3.90 (t,  $J = 7$  Hz, 4 H) and 2.1-2.9 (m, 4 H);  $^{19}\text{F}$  NMR  $\delta$  -74.4 (3 F), -112.9 (2 F), 117.4 (2 F), 120.1-121.0 (4 F), 123.3 (2 F) and 182.1 (1 F); IR (neat) 3400, 3050, 2975, 1040-1340, and 980  $\text{cm}^{-1}$ . *Anal.* Calcd for  $\text{C}_{11}\text{H}_{10}\text{F}_{14}\text{O}_2$ : C, 30.01; H, 2.29; F, 60.43. Found: C, 30.04; H, 2.36; F, 60.42.

**Diols from Ethylene adducts of 1:2 1,4-Diiodoperfluorobutane-Perfluoropropylene Telomers.** Reaction of the ethylene insertion products of the 1:2 1,4-diiodoperfluorobutane-perfluoropropylene telomers (4.6 g, 5.7 mmol) with 30% fuming sulfuric acid (50 mL) by the above method gave 2.6 g (76%) of the corresponding diols after Kugelrohr distillation (124-130 °C, 0.5 mm):  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  3.83 (t,  $J = 7$  Hz, 4 H) and 2.50 (m, 4 H);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -68.5, -74.2, -109.8, -111.1, -112.8, -117.2, -119.1, -119.8, -120.9, -123.1, and -182.0; IR (neat) 3400, 3050, 2975, 1040-1400, and 1000  $\text{cm}^{-1}$ . *Anal.* Calcd for  $\text{C}_{14}\text{H}_{10}\text{F}_{20}\text{O}_2$ : C, 28.49; H, 1.71; F, 64.38. Found: C, 28.65; H, 1.69; F, 64.64.

**Diols from 1:3 1,4-Diiodoperfluorobutane-Perfluoropropylene Telomers.** Reaction of the ethylene insertion products of the 1:3 telomers of 1,4-diiodoperfluorobutane and perfluoropropylene (5.0 g, 5.2 mmol) with 30% fuming sulfuric acid (26 mL) by the above method gave 2.8 g (73%) of the corresponding diols after Kugelrohr

distillation (150-155 °C, 0.3 mm):  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  3.79 (br m, 4 H) and 2.58 (br m, 4 H);  $^{19}\text{F}$  NMR  $\delta$  -65.4 to -70.3 (9 F), -105.1 to -118.7 (14 F), and -175.8 to -177.6 (3 F); IR (neat) 3450, 2975, 1040-1400, and 1000  $\text{cm}^{-1}$ . *Anal.* Calcd for  $\text{C}_{17}\text{H}_{10}\text{F}_{26}\text{O}_2$ : C, 27.58; H, 1.36. Found: C, 27.13; H, 1.31.

### 3-Trifluoromethyl-3,4,4,5,5,6,6,7,7,8,8-undecafluorodecane-1,10-diol:

**Nitric Acid Procedure.** A mixture of 100%  $\text{HNO}_3$  (10 mL) and 1,10-diiodo-3-trifluoromethyl-3,4,4,5,5,6,6,7,7,8,8-undecafluorodecane (14 g, 21.2 mmol) was heated at 65 °C for 8 h. The progress of the reaction was monitored by  $^1\text{H}$  NMR spectroscopy. The bottom layer was separated and washed with water to give 10 g (89%) of dinitrate ester:  $^1\text{H}$  NMR  $\delta$  4.76 (m, 4 H) and 2.62 (m, 4 H);  $^{19}\text{F}$  NMR -75.3, -113.6, -117.8, -120.9, -121.6, and -123.7. The crude product was then added, dropwise over a 30 min period, to a stirred mixture of acetic anhydride (20 mL) and concentrated sulfuric acid (0.8 mL) at room temperature. After an induction period of 5 min, an exothermic reaction resulted in a temperature increase of 70 °C in a few minutes. The reaction mixture was cooled with an ice bath and when the exotherm subsided, the mixture was quenched with ice. The bottom layer was separated, dissolved in diethyl ether, washed with 10% sodium bicarbonate and brine, and dried ( $\text{MgSO}_4$ ). Solvent was removed under reduced pressure to give the diacetate:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.36 (m, 4 H), 2.45 (m, 4 H), and 2.07 (s, 6 H). The diacetate was dissolved in a mixture of methanol (20 mL) and concentrated sulfuric acid (1 mL), and the mixture was heated under reflux for 16 h. Solvent was removed under reduced pressure, and the residue was partitioned between equal amounts of diethyl ether and 10%  $\text{H}_2\text{SO}_4$ . The organic

layer was washed with brine, dried, and concentrated under reduced pressure to give 3.95 g (52%) of 3-trifluoromethyl-3,4,4,5,5,6,6,7,7,8,8-undecafluorodecane-1,10-diol.

**1,10-Diazido-3-trifluoromethyl-3,4,4,5,5,6,6,7,7,8,8-undecafluorodecane.**

Care should be exercised in the handling of aliphatic azides. No problems were encountered in these preparations, but the materials should be considered potentially explosive. Sodium azide (0.30 g, 4.6 mmol) was added over a 4 h period to a solution of 1,10-diiodo-3-trifluoromethyl-3,4,4,5,5,6,6,7,7,8,8-undecafluorodecane (1.1 g, 1.7 mmol) in a mixture of freshly distilled DMSO (18 mL) and THF (5 mL). The mixture was stirred at room temperature for 16 h and additional sodium azide (0.15 g, 2.3 mmol) was added. The mixture was stirred for an additional 24 h, diluted with diethyl ether and poured over crushed ice and water. The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic solutions were washed with water, aqueous sodium sulfite and brine and dried ( $\text{MgSO}_4$ ), and stripped of solvent under reduced pressure. Glc and NMR indicated that the crude product contained ca. 13% of elimination products. Distillation gave a forerun, bp 50-75 °C (0.1 mm), containing elimination products, and 0.46 g (55%) of 1,10-diazido-3-trifluoromethyl-3,4,4,5,5,6,6,7,7,8,8-undecafluorodecane: bp 85-100 °C (0.1 mm); IR ( $\text{CDCl}_3$ ) 3050, 2975, 2150 (s), and 1100-1380  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.46 (t,  $J = 6$  Hz, 4 H) and 2.30 (m, 4 H). *Anal.* Calcd for  $\text{C}_{11}\text{H}_8\text{F}_{14}\text{N}_6$ : C 26.95; H, 1.64. Found: C, 27.07; H, 1.67.

**Azides from Ethylene Adducts of 1:2 1,4-Diiodoperfluorobutane-Perfluoropropylene Telomers.** Sodium azide (1.2 g, 18.5 mmol) was added to a suspen-

sion of 1:2 of 1,4-diiodoperfluorobutane-perfluoropropylene telomers (7.0 g, 8.6 mmol) in DMSO (67 mL, freshly distilled) and THF (23 mL) and the mixture was stirred at room temperature for 20 h. A second portion of sodium azide (1.3 g, 20 mmol) was added. After 24 h, the product was worked up as in the above example. Distillation gave a forerun at (bp 70-80 °C, 0.1 mm), that contained olefins, followed by 3.1 g (56 %) of the title diazides: bp 90-120 °C (0.1 mm), IR (CDCl<sub>3</sub>) 3050, 2975, 2150 (s), and 1100-1400 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.46 (t, J = 6 Hz, 4 H) and 2.36 (m, 4 H). The material was used without further purification for preparation of the corresponding diamines.

**1,10-Diamino-3-trifluoromethyl-3,4,4,5,5,6,6,7,7,8,8-undecafluorodecane.** A solution of hydrazine (1.15 g, 36 mmol) in methanol (5 mL) was added, dropwise with stirring, under nitrogen, to a mixture of 1,10-diazo-3-trifluoromethyl-3,4,4,5,5,6,6,7,7,8,8-undecafluorodecane (7.2 g, 14.7 mmol), methanol (40 mL), and Pearlman's catalyst, palladium hydroxide on carbon, (0.6 g) and the mixture was refluxed for 21 h. The mixture was filtered through a pad of celite. Solvent was removed and the residue was distilled to give 2.5 g (39%) of 1,10-diamino-3-trifluoromethyl-3,4,4,5,5,6,6,7,7,8,8-undecafluorodecane, a colorless oil: bp 85-95 °C (0.2 mm); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.0 (t, J = 6 Hz, 4 H), 2.20 (m, 4 H) and 1.23 (s, 4 H). *Anal.* Calcd for C<sub>11</sub>H<sub>12</sub>F<sub>14</sub>N<sub>2</sub>: C, 30.15; H, 2.76; F, 60.70. Found: C, 29.85; H, 2.36; F, 60.32.

**Reduction of Azides Derived from Ethylene adducts of 1:2 1,4-Diiodoperfluorobutane:Perfluoropropylene Telomers .** The mixture of azides prepared from

ethylene adducts of the 1:2 1,4-diiodoperfluorobutane:perfluoropropylene telomers (2.9 g, 4.5 mmol), dissolved in methanol (30 mL) was hydrogenated (25 °C, 24 h, 30 psi) in a Parr apparatus, using Pearlman's catalyst (0.5 g). The mixture was diluted with methanol, filtered through celite, stripped of solvent, and Kugelrohr distilled (105-120 °C, 0.3 mm) to give 0.90 g (35%) of diamines: IR 3350, 3050, 2975, and 1000-1380  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  2.92 (t,  $J = 6$  Hz, 4 H), 2.20 (m, 4 H) and 1.26 (s, 4 H). *Anal.* Calcd for  $\text{C}_{14}\text{H}_8\text{F}_{20}\text{N}_2$ : C, 28.59; H, 2.05; F, 64.60. Found: C, 28.90; H, 2.07; F, 64.32.

**3-Trifluoromethyl-3,4,4,5,5,6,6,7,7,8,8-undecafluorodecane-1,10-diisocyanate.** Hydrogen chloride was bubbled through a suspension of 1,10-diamino-3-trifluoromethyl-3,4,4,5,5,6,6,7,7,8,8-undecafluorodecane (3.0 g, 6.8 mmol) in 1,2-dichlorobenzene (50 mL) for 1 h. Phosgene was bubbled through into the mixture and the temperature was increased gradually to 135 °C. The formation of a homogeneous solution indicated completion of the reaction. Phosgene was flushed from the mixture with argon and 1,2-dichlorobenzene was removed by distillation (30-32 °C, 0.2 mm). The residue was Kugelrohr distilled (130-140 °C, 0.2 mm) to give 1.7 g (51%) of 3-trifluoromethyl-3,4,4,5,5,6,6,7,7,8,8-undecafluorodecane-1,10-diisocyanate:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.55 (m, 4 H) and 2.33 (m, 4 H);  $^{19}\text{F}$  NMR  $\delta$  -75.2 (3 F), -114.65 (2 F), -117.96 (2 F), -120.9 (2 F), -121.65 (2 F), -123.88 (2 F), and -85.25 (1 F). *Anal.* Calcd for  $\text{C}_{13}\text{H}_8\text{F}_{14}\text{N}_2\text{O}_2$ : C, 31.85; H, 1.64; N, 5.71. Found: C, 31.74; H, 1.45; N, 5.66.

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## References and Notes

1. Goethals, E. J., ed., *Telechelic Polymers: Synthesis and Applications*, CRC Press, Boca Raton, Florida, 1988.
2. Heitz, W. *Angew. Makromol. Chem.* 1986, 145-6, 37-68.
3. Jerome, R.; Henriouille-Granville, M.; Boutevin, B.; Robin, J. J. *Prog. Polym. Sci.* 1991, 16, 837-906.
4. Boutevin, B.; Robin, J. J. *Adv. Polym. Sci.* 1992, 102, 105-131.
5. Bedford, C. D.; Baum, K. *J. Org. Chem.* 1980, 45, 347.
6. Haszeldine, R. N. *Nature (London)* 1951, 167, 139.
7. Baum, K.; Bedford, C. D.; Hunadi, R. J. *J. Org. Chem.* 1982, 47, 2251.
8. Knunyants, I. L.; Khrlakyan, S. P.; Zeifman, Yu. V.; Shokina, V. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1964, 2, 384.
9. Rondestvedt, C. S. *J. Org. Chem.* 1977, 42, 1985.
10. Mares, F.; Oxenrider, B. C. *J. Fluorine Chem.* 1976, 8, 373.
11. Malik, A. A.; Tzeng, D.; Cheng, P.; Baum, K. *J. Org. Chem.* 1991, 56, 3043-4.
12. Hauptschein, M.; Braid, M.; Lawler, F. E. *J. Am. Chem. Soc.* 1957, 79, 2549.
13. Tortelli, V.; Tonelli, C. *J. Fluorine Chem.* 1990, 47, 199-217.
14. Takamura, T.; Yamabe, M.; Kato, M. *J. Fluorine Chem.* 1988, 41, 173.
15. Brace, N. O. *J. Fluorine Chem.* 1986, 31, 151.
16. Rebsdats, S.; Schuierer, E.; Ulm, K.; Wimmer, I. *Ger. Pat.* 2,028,459, 1971; *Chem. Abst.* 1972, 76, 58963b.

17. Honeychuck, R. V.; Ho, T; Wynne, K. J.; Nissan, R. A. *Chem. of Materials* 1993, 5, 1299-1306.
18. Sriver, E. F.; Turnbull, K. *Chem. Rev.* 1988, 88, 1985.
19. Malik, A. A.; Preston, S. B.; Archibald, T. G.; Cohen, M. P.; Baum, K. *Synthesis* 1989, 450.